

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-000894  
 (43)Date of publication of application : 07.01.2000

(51)Int.CI.

 B29C 67/20  
 C08J 3/12  
 // B29K101:12  
 B29K105:04

(21)Application number : 10-168327

(71)Applicant : MITSUBISHI KAGAKU FORM PLASTIC KK

(22)Date of filing : 16.06.1998

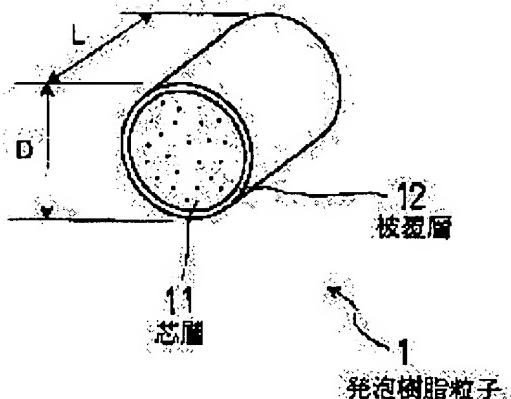
(72)Inventor : YOKOYAMA MASAAKI  
OKUWA TERUYA

## (54) PRODUCTION OF THERMOPLASTIC RESIN FOAM MOLDING

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a method for producing a thermoplastic resin foam molding having good shape stability and high fusion strength in foamed resin particles.

**SOLUTION:** A molding comprises foamed core layer 11 of a crystalline thermoplastic resin and substantially nonfoamed cover layer 12 covering the core layer 11. The cover layer contains an ethylene polymer the melting point of which is lower than that of the thermoplastic resin or is latent. A process in which foamed resin particles 1 in which the ratio L/D between the long diameter L and the short diameter D of the particle is 0.5-3 are prepared and process in which the resin particles are placed in a molding mold and heated/ molded by hot blast to be fused together in order to obtain a foamed molding are included. A dry gas of 5 kPa or below steam pressure is used as the hot blast.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1] While becoming the real target which covers the core layer and this core layer of the foaming state which consists of crystalline thermoplastics from the enveloping layer in the state where it does not foam, this enveloping layer The melting point in a low from the above-mentioned thermoplastics Or the process for which the ethylene system polymer which does not show the melting point substantially is contained, and the foaming resin particle whose ratio-of-length-to-diameter ratios of the major axis L of a particle and a minor axis D are 0.5-3 is prepared, By putting in this foaming resin particle in a form block, and carrying out hot forming by hot blast It is the manufacture method of a thermoplastics foaming object that it consists of a process which acquires the thermoplastics foaming object which made the above-mentioned foaming resin particle weld mutually, and the above-mentioned hot blast is characterized by a water vapor pressure using the dry gas of 5 or less kPas.

[Claim 2] It is the manufacture method of the thermoplastics foaming object characterized by for hot forming of the above-mentioned foaming resin particle compressing the bulk of this foaming resin particle to 50 - 95% in a claim 1, and carrying out where apparent density gravity is made high.

[Claim 3] It is the manufacture method of the thermoplastics foaming object characterized by performing hot forming of the above-mentioned foaming resin particle at the temperature of 125 degrees C or less in a claim 1 or 2.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] this invention relates to the manufacture method of the thermoplastics foaming object used for a heat insulator, shock absorbing material, a packing container, acoustic material, floatage material, etc.

#### [0002]

[Description of the Prior Art] The foaming object which consists of thermoplastics, such as polystyrene, polyethylene, and polypropylene, is used for a heat insulator, shock absorbing material, a packing container, acoustic material, and floatage material. This foaming object has closed-cell structure, is lightweight, and is good. [ of adiathermancy or buffer nature ] These foaming resin particles are hard to be heated uniformly at the time of this adiathermancy, therefore hot forming, and the point of manufacturing the foaming object using the steam with large heat capacity as a heating medium is common. A foaming resin particle is put into metal mold, and a foaming object heats it, and is fabricated by making a particle front face weld. In order to make a resin particle comrade weld, as the former and vapor pressure, with polystyrene, the steam of 0.5 or less MPas was used by 0.1 or less MPas, and was used with 0.2 or less MPas and polypropylene with polyethylene.

#### [0003]

[Problem(s) to be Solved] However, by the welding method by the above-mentioned conventional steam heating, at the time of heating weld, if moisture permeates by the gaseous state into the opening of a foaming resin particle, or a particle and it cools in this state, moisture will condense in the state of a liquid from a gas, and a volumetric shrinkage will be started. For this reason, the foaming object with which the inside of the opening of a foaming resin particle or a particle will be in a reduced pressure state, and consists of this particle will contract and deform, and there is a problem that configuration stability is bad and a formal Plastic solid is hard to be obtained. Moreover, in a foaming object, a foaming resin particle fully welds and it is required that a mechanical strength should also be high.

[0004] In view of this conventional trouble, it excels in configuration stability and this invention tends to offer the manufacture method of a thermoplastics foaming object that the weld intensity in a foaming resin particle is high.

#### [0005]

[Means for Solving the Problem] While this invention becomes the real target which covers the core layer and this core layer of the foaming state which consists of crystalline thermoplastics from the enveloping layer in the state where it does not foam, this enveloping layer The process for which the melting point is lower than the above-mentioned thermoplastics, the ethylene system polymer which does not show the melting point substantially is contained, and the foaming resin particle whose ratio-of-length-to-diameter ratios of the major axis L of a particle and a minor axis D are 0.5-3 is prepared, By putting in this foaming resin particle in a form block, and carrying out hot forming by hot blast It is the manufacture method of a thermoplastics foaming object that it consists of a process which acquires the thermoplastics foaming object which made the above-mentioned foaming resin particle weld mutually, and a water vapor pressure is characterized by using the dry gas of 5 or less kPas, as for the above-mentioned hot blast.

[0006] The manufacture method of the thermoplastics foaming object in this invention uses like the above the foaming resin particle which consists of a specific core layer and an enveloping layer which covers this. Therefore, it is the epoch-making method that a foaming object can be acquired by heating in the hot blast which does not use at all the steam (steam) conventionally used as a heating medium, but consists of the above-mentioned dry gas.

[0007] An operation and effect of this invention are explained. A foaming resin particle is put in in a form block, and is carrying out hot forming to the request configuration using the hot blast which consists of the above-mentioned dry gas. Therefore, into the opening of a foaming resin particle, or a particle, a steam hardly permeates at the time of hot forming. So, the water of the Plastic solid by condensation of the steam which was the conventional fault is also exhausted, and the volumetric shrinkage of the Plastic solid accompanying it does not happen, either. Therefore, the foaming resin Plastic solid of this invention is excellent in configuration stability. Moreover, the elevated-temperature care-of-health processing for correcting a size and contraction deformation is also unnecessary. And since there is also no water, it is not necessary to carry out dryness processing after fabrication, and the acquired foaming object is excellent in adiathermancy, and does not have fear of rust generating, either. Moreover, the metal mold which has the weight of structure conventionally which bears the high-pressure vapor pressure used at the time of hot forming of the conventional foaming resin particle in hot forming by the dry gas is unnecessary, and the consumption of heat energy also has it. [ little ]

[0008] Moreover, since it loses the influence by the moisture of a steam in really fabricating within a mold, the epidermis and

foaming resin particle which consist of thermoplastics weld firmly the epidermis and foaming resin particle which consist of thermoplastics. Therefore, the foaming object acquired by this invention has high weld intensity, and is excellent in the mechanical strength. Moreover, when the textile fabrics or the nonwoven blanket-like one which consists of thermoplastics as epidermis is used, the failure by hair on the front face of epidermis generated at the time of steam iron credit is lost, appearance, such as tone and a feel, is also good, a process also becomes unnecessary after dryness, and it is industrially advantageous.

[0009] In addition, as epidermis, the shape of the shape of a film and a sheet, a vacuum-forming article, injection mold goods, etc. can also a foaming resin particle and really be fabricated.

[0010] Moreover, the foaming resin particle is constituted from a film-like enveloping layer by the core layer which is the closed-cell object which consists of crystalline thermoplastics, and the real target containing an ethylene polymer. Therefore, suppressing the foaming force of a core layer with the melting point higher than an enveloping layer by making the opening between the foaming resin particles with which it filled up in the mold pass hot blast with small heat capacity, a foaming resin particle can be heated to temperature required for an enveloping layer to weld, the compression reaction force which a core layer holds can be utilized effectively after that, a foaming resin particle can be made to be able to weld, and a foaming object can be manufactured.

[0011] Next, the detail of this invention is explained.

(Preparation of a foaming resin particle) The foaming resin particle in this invention has the core layer of a foaming state, and the composite construction which consists of enveloping layers in the state where it does not foam, substantially. The core layer of a foaming state has for example, closed-cell structure or open-cell structure. Among this, it is desirable to have closed-cell structure. The reason is that closed-cell structure has the high compression reaction force of the core layer at the time of hot forming, and compressive strength is high also by low density. 50% or more of the rate of a closed cell of a core layer is desirable, and it is desirable that it is 70 more% or more. The compression reaction force of the core layer at the time of hot forming becomes still higher by this, and a foaming object with high compressive strength can be acquired also by low density. An enveloping layer is in the state where it does not foam. As for an enveloping layer, it is desirable that it is the thermoplastics layer of the shape of a film with a thickness of 1-150 micrometers.

[0012] A core layer consists of crystalline thermoplastics. As this crystalline thermoplastics, a polypropylene regin, a polybutene system resin, the poly methyl pentene system resin, a polyester system resin, a polyamide system resin, a fluorine system resin, a crystalline styrene resin, etc. are mentioned, for example. Also in this, a propylene homopolymer, and the random copolymers and block copolymers with an alpha olefin other than a propylene and a propylene are desirable. By this, it is cheap and excels in recycling nature, and it can be lightweight and the foaming object excellent in adiathermancy and buffer nature can be acquired.

[0013] An enveloping layer is in the state where it does not foam, substantially. "It is the state where it does not foam, substantially" is as thin as 1-150 micrometers in thickness, and it means a film state without cellular structure. Moreover, the melting point of an enveloping layer is lower than the above-mentioned thermoplastics, or it contains the ethylene system polymer which does not show the melting point substantially. As this ethylene system polymer of the low melting point, the copolymer of vinyl acetate besides a high-pressure-process low density polyethylene, a straight chain-like low density polyethylene, and a straight chain-like super-low density polyethylene, an unsaturation carboxylate, a unsaturated carboxylic acid, vinyl alcohol, etc. and ethylene is mentioned.

[0014] When a temperature up is carried out to "there is no melting point substantially" with a differential scanning calorimeter, a resin without the crystallinity in which a dissolution peak does not appear is meant. As this ethylene system polymer that does not have the melting point substantially, rubber elastomers, such as ethylene-propylene rubber, ethylene propylene diene rubber, an ethylene acrylic rubber, chlorinated-polyethylene rubber, and chlorosulfonated polyethylene rubber, are mentioned, for example. These ethylene system polymers can be used as two sorts or more besides independent use of constituents.

[0015] In the above-mentioned ethylene system polymer, a high-pressure-process low density polyethylene, a straight chain-like low density polyethylene, and a straight chain-like super-low density polyethylene are desirable. The straight chain-like low density polyethylene and the straight chain-like super-low density polyethylene by which the polymerization was carried out especially using the metallocene catalyst are the most desirable.

[0016] As for the melting point of the above-mentioned ethylene system polymer which constitutes an enveloping layer, it is desirable that it is 125 degrees C or less though there is nothing substantially or there is the melting point. The reason is that it can set more the heating temperature at the time of fabricating a foaming resin particle as low temperature.

[0017] Furthermore, it is desirable to use it as an enveloping layer to the thermoplastics which constitutes a core layer, choosing the ethylene system polymer of the melting point low 15 degrees C or more. The range of the above-mentioned melting point difference of an ethylene system polymer and thermoplastics is 20 degrees C - 100 degrees C preferably. When the above-mentioned melting point difference is less than 15 degrees C, there is a possibility that the enveloping layer which consists of an ethylene system polymer under the condition on which the thermoplastics of a core layer is made to foam may foam.

[0018] Moreover, as for the above-mentioned enveloping layer, it is desirable that it is the mixture of the above-mentioned ethylene system polymer, and a core layer and crystalline thermoplastics of the same kind. Thereby, the adhesive property of an enveloping layer and a core layer improves. As for the blending ratio of coal of the thermoplastics in an enveloping layer, it is desirable to be chosen from the range of the 1 - 100 weight section to the ethylene system polymer 100 weight section.

When the blending ratio of coal of thermoplastics is under 1 weight section, there is a possibility that the effect of adhesive improvement with a core layer and an enveloping layer may become low. Moreover, in exceeding the 100 weight sections, the \*\*\*\* form of an enveloping layer will change, the phase of the sea where thermoplastics continued will be constituted, and the heating temperature at the time of fabrication does not become not much low. Furthermore, as for the mixed rate of thermoplastics, it is desirable that it is the range of 1 - 50 weight section to the ethylene system polymer 100 weight section. Thereby, the adhesive property of a core layer and an enveloping layer can improve, and heating temperature at the time of fabrication can be made low.

[0019] As for the thickness of an enveloping layer, in a foaming resin particle, it is desirable that it is 1-150 micrometers. When the thickness of an enveloping layer is less than 1 micrometer, there are few effects of fully reducing heating temperature, in the case of fabrication. On the other hand, when the thickness of an enveloping layer exceeds 150 micrometers, in the case of fabrication, substantially, the rate of an un-foaming nature portion is large, and heating temperature has the mechanical strength of a Plastic solid in the inclination in the enveloping layer of what can be lowered which becomes low considering an expansion ratio. Furthermore, as for the thickness of an enveloping layer, it is desirable that it is 10-100 micrometers. Thereby, heating temperature can be lowered in the case of fabrication, and the mechanical strength of a foaming object can be raised.

[0020] As shown in drawing 1, the ratio-of-length-to-diameter ratios of the major axis L of the foaming resin particle 1 of this invention and a minor axis D are 0.5-3. The surface area of an enveloping layer 12 decreases in the case of less than 0.5, and poor weld is brought to it. Moreover, in exceeding 3, a particle shape serves as \*\* length, a charging efficiency gets worse, and it brings about the fall of poor forming and configuration stability. Although a ratio-of-length-to-diameter ratio becomes easy to obtain 1.5-3, and a Plastic solid with many [ when comparatively large ] openings, it is desirable from the point of a moldability that it is 0.8-2.

[0021] As shown in drawing 1, after infiltrating an volatile foaming agent into the complex particle which consists of a core layer 11 which consists of crystalline thermoplastics, and an enveloping layer 12 containing the ethylene system polymer which the melting point is lower than thermoplastics, or does not show the melting point substantially, the above-mentioned foaming resin particle 1 carries out heating foaming, and is obtained.

[0022] as the above-mentioned volatile foaming agent, inorganic gas, such as halogenated hydrocarbons, such as low-grade aliphatic hydrocarbon, such as a propane, butane, a pentane, a heptane, a cyclopentane, and a cyclohexane, dichloro JIFURORO methane, and TORIKUROROMONOFURORO methane, nitrogen, air, and carbon dioxide gas, etc. mentions -- having -- that these are independent or two kinds -- with, the Kamigumi \*\*\*\*\* use is carried out

[0023] The following all directions method is used as the concrete manufacture method of the complex particle used as the raw material of a foaming resin particle. For example, the \*\*\*\* type compound die of a publication is used for JP,41-16125,B, a 43-23858 official report, a 44-29522 official report, JP,60-185816,A, etc. In this case, after using two sets of extruders, carrying out melting kneading of the thermoplastics which constitutes a core layer from one extruder and carrying out melting kneading of the ethylene system polymer constituent which constitutes an enveloping layer from an extruder of another side, thermoplastics is used as a core layer with a die, and \*\*\*\* type complex is made to breathe out by making an ethylene system polymer constituent into an enveloping layer.

[0024] Subsequently, the complex obtained by making it this appearance is cut, and it considers as a 0.1-10mg complex particle. Since the enveloping layer ratio into which the heating temperature of a fabricating operation is reduced effectively becomes high when the weight of a complex particle is less than 0.1mg, the mechanical strength of the foaming object acquired falls. On the other hand, when the weight of a complex particle exceeds 10mg, the restoration nature to the metal mold at the time of fabrication tends to get worse.

[0025] After sinking an volatile foaming agent into an above \*\*\*\* type complex particle, it is made to foam by heating. Specifically as this heating foaming method, the method of a publication can be used for JP,49-2183,B, a 56-1344 official report, the West Germany provisional-publication-of-a-patent No. 1285722 official report, a 2107683 official report, etc.

[0026] in this case, a \*\*\*\* type complex particle is put in with an volatile foaming agent in an airtight container, and it heats more than the softening temperature of the crystalline polymer of a core layer -- an volatile foaming agent is both infiltrated into a complex particle Then, after emitting the contents in an airtight container to a low-pressure atmosphere from an airtight container, a foaming resin particle is obtained by carrying out dryness processing.

[0027] Usually, although heating temperature at the time of foaming of a complex particle is carried out to more than the softening temperature of the thermoplastics of a core layer, it is desirable to make it temperature higher than the melting point (it is the melting point of a principal component in the case of a constituent) of the ethylene system polymer of an enveloping layer. Moreover, since complex particles are made to act mutually in an airtight container as a \*\* person in this invention, it is desirable to \*\*\*\* stirring equipment.

[0028] It is desirable to use water, alcohols, etc. as a dispersion medium of a complex particle at the time of heating foaming of a complex particle. Furthermore, it is desirable independent or that two or more kinds use anionic detergents, such as water-soluble protective colloid, such as a mineral matter of difficulty water solubility of an aluminum oxide, the third calcium phosphate, pyrophosphoric-acid magnesium, a zinc oxide, etc., a polyvinyl pyrrolidone, polyvinyl alcohol, and a methyl cellulose, sodium dodecylbenzenesulfonate, and alpha olefin sulfonic-acid sodium, mixing so that a complex particle may distribute uniformly to a dispersion medium.

[0029] As for a complex particle, emitting to low voltage atmosphere is desirable. Thereby, the thermoplastics of a complex particle can foam and the foaming resin particle which consists of a core layer of a foaming state and an enveloping layer

which covers this can be obtained. In case a complex particle is emitted to a low-pressure atmosphere, in order to make the discharge concerned easy, it is desirable to introduce the same inorganic gas as the above or an volatile foaming agent into an airtight container from the exterior, and to hold the pressure in an airtight container uniformly.

[0030] As for a foaming resin particle, the thermoplastics of a core layer presents the foaming state of closed-cell structure from the state of the cut cross section of the particle, and, on the other hand, the ethylene system polymer of an enveloping layer is in the film state where it does not foam, substantially.

[0031] (Hot forming of a foaming resin particle) Hot forming of the foaming resin particle is carried out in hot blast. Here, hot blast heats air by heating meances, such as an electrical heater and a steamy heater, and is acquired. Moreover, if it supplies using a blower and the compressed air, a foaming resin particle can be heated efficiently. Moreover, the loss of heat energy can be lessened by using the method which collects hot blast and circulates.

[0032] As for hot blast, a water vapor pressure uses the dry gas of 5 or less kPas. Thereby, at the time of hot forming, it can prevent that a steam permeates into the opening of a foaming resin particle, or a particle, and the configuration stability of a foaming object can be secured.

[0033] Moreover, as for the temperature of the foaming resin particle at the time of hot forming, it is desirable that it is 125 degrees C or less. It is because there is a possibility that it may also become more difficult for the generator of hot blast to be large, and to become expensive, and for a industrial merit to be lost, and to carry out heating control of the foaming resin particle in a mold uniformly when exceeding 125 degrees C.

[0034] In case hot forming of the foaming resin particle is carried out, although the compression state of a foaming resin particle is suitably set up by the physical properties required of a Plastic solid, if compression is made small, the Plastic solid in which a few opening has the touch area of foaming resin particles will be obtained. Moreover, heating and compression may perform any first.

[0035] As for hot forming of a foaming resin particle, it is desirable to compress the bulk of this foaming resin particle to 50 - 95%, and to carry out, where apparent density gravity is made high. In compressing to 50% or more, the foaming object in the state where there is almost no opening will be acquired, and it is meaningless only by merely only enlarging density of a foaming object. In compressing to less than 95%, the touch area of foaming resin particles becomes smaller, and becomes a foaming object with weak weld intensity.

[0036] As the concrete method of hot forming of a foaming resin particle For example, making the gap between the foaming resin particles 1 with which it filled up in (a) and female mold 211 pass hot blast 5, as shown in drawing 2, after being filled up with the foaming resin particle 1 in the female mold 211 of permeability There is a way the enveloping layer which constitutes a foaming resin particle for the skin temperature of the foaming resin particle 1 heats to temperature required to weld, compresses the bulk of the foaming resin particle 1 to 50 - 95% by (b) and its Gokami type 212, and acquires (c) foaming object 3.

[0037] Moreover, as shown in drawing 3, into the metal mold 22 of sealing nature, where it compressed the bulk of the foaming resin particle 1 to 50 - 95% and it is held, put in a foaming resin particle, and hot blast pressurization gas 51 is pressed fit (a) and into it. the enveloping layer which the gap between the foaming resin particles 1 is made to pass hot blast pressurization gas 51, and constitutes a foaming resin particle for the skin temperature of the foaming resin particle 1 -- up to temperature required to weld -- heating -- (b) -- subsequently There is a method of acquiring the foaming object 3 (c) by discharging hot blast pressurization gas 51 and recovering the compression state of the foaming resin particle 1.

[0038] In this invention, although a process condition is chosen in consideration of the character of a foaming resin particle, the configuration of a foaming object, density, etc., it processes beforehand by the volatile foaming agent or inorganic gas, and if the foaming resin particle which heightened the secondary foaming force is used, a foaming object with more small density will become is easy to be acquired. Moreover, manufacture of a tabular foaming object is also possible by replacing with the mold of an uneven couple with permeability, and using a belt with permeability.

[0039] It is the thermoplastics foaming object which comes to carry out hot forming of the foaming resin particle which consists of a core layer of the foaming state which consists of crystalline thermoplastics as a thermoplastics foaming object acquired by the above-mentioned manufacture method, and an enveloping layer which covers this core layer, and the above-mentioned enveloping layer is the thermoplastics foaming object which the melting point is low than the above-mentioned thermoplastics, contains the ethylene system polymer which does not show the melting point substantially, and is characterized by to be in the state do not foam.

[0040] the thermoplastics foaming object acquired by this invention -- for example, a heat insulator, shock absorbing material, a packing container, acoustic material, floatage material, and industry -- it is used for a member etc. Moreover, a thermoplastics foaming object is used for one mold goods with the textile fabrics and the nonwoven fabric which consist of thermoplastics, a film, a sheet, a vacuum-forming article, and injection mold goods etc.

[0041]

[Embodiments of the Invention] The example of an operation form of this invention is explained comparing examples 1-3 with the examples 1-4 of comparison.

The ethylene propylene random copolymer (153 degrees C of melting points) of 1.5 % of the weight of ethylene contents was kneaded using the monopodium extruder with example 1 bore of 40mm, and the straight chain-like low density polyethylene (91 degrees C of melting points) by which the polymerization was carried out with the metallocene catalyst of density 0.895 using the monopodium extruder with a bore of 25mm was kneaded. Subsequently, from the die which has a die orifice with a diameter of 1.5mm, the ethylene propylene random copolymer was used as the core layer, and the strand was extruded by

making a straight chain-like low density polyethylene into an enveloping layer.

[0042] Furthermore, this strand was cut to 1.2mg, after cooling through a tank. When the cross section of this complex particle was observed with the phase-contrast microscope, the straight chain-like low density polyethylene with a thickness of 30 micrometers had covered the ethylene propylene random copolymer.

[0043] Next, in the airtight container, the above-mentioned complex particle 100 weight section, the water 250 weight section, the third calcium phosphate 1.0 weight section with a particle size of 0.3-0.5 micrometers, and the sodium dodecylbenzenesulfonate 0.007 weight section were taught, and, subsequently the butane 20 weight section was supplied into the airtight container under stirring. After filling up contents with 62% of filling factors, the temperature up was carried out to 145 degrees C over 1 hour, and it held for 30 minutes at this temperature.

[0044] then, the discharge in the bottom of an airtight container -- having introduced nitrogen gas to the gaseous-phase section in an airtight container, and holding the pressure in \*\*\*\* from the exterior, while opening the valve of a hole, bottom HE discharge of atmospheric pressure of the contents was carried out, and the foaming resin particle was obtained In this way, the obtained foaming resin particles are average bulk density 17 kg/m<sup>3</sup> and 120 micrometers of diameters of average air bubbles, and did not have blocking of foaming resin particles, either.

[0045] When the cross section of this foaming resin particle was observed with the phase-contrast microscope, the ethylene propylene random copolymer of a core layer was in the foaming state of a closed cell, and on the other hand, a straight chain-like low density polyethylene is in the film state where it does not foam, substantially, and had covered the core layer of the foaming state of an ethylene propylene random copolymer. ratio of length to diameter of the major axis L of a foaming resin particle and a minor axis D is 0.9.

[0046] This foaming resin particle is dried completely [ in 40-degree C drying room ], the gap between the foaming resin particles with which it filled up in the mold after being filled up with this foaming resin particle in the mold of an uneven couple with permeability was made to pass hot blast, the skin temperature of a foaming resin particle was heated at 120 degrees C, and, subsequently to 60%, the foaming resin particle was made to weld, where mold content volume is reduced. Then, it cooled with air and the foaming object was taken out from the inside of a mold. The density of the foaming object was 28 kg/m<sup>3</sup>, and the size was 40mm in the length of 200mm, width of face of 300mm, and thickness, and was a formal configuration which does not have water, either and does not have contraction deformation.

[0047] When 20 pieces of test pieces with a length of 200mm, a width [ of 30mm ], and a thickness of 12.5mm were produced, it wound around the periphery of a cylinder with a diameter of 50mm and it bent from the above-mentioned foaming object to the angle of 90 degrees, 80% or more of a test piece did not break.

[0048] In examples 2 and 3, one to example of comparison 4 examples 2 and 3, and the examples 1-4 of comparison, as shown in Table 1, the resin of the resin of a core layer and a state, and an enveloping layer and a state, average bulk density, a ratio-of-length-to-diameter ratio, a heating medium, hot-forming temperature, and compressibility were changed, and the foaming object was manufactured. Others were manufactured like the example 1.

[0049] About the physical properties of the above-mentioned examples 1-3 and the examples 1-4 of comparison, it measured by the following methods.

It measured with the <melting point> differential scanning calorimeter (DSC). First, it cooled to the room temperature the speed for 10-degree-C/after the temperature up to the temperature to which the \*\*\*\* dissolves a 3-5mg resin. Subsequently, the heating temperature up was carried out the speed for 10-degree-C/, and it considered as the melting point with the peak temperature of the endothermic curve obtained.

[0050] The weight ratio per unit volume of a <Plastic-solid density> foaming object was measured.

3l. of water was put in in the measuring cylinder with a graduation with a <voidage> bore [ of 150mm ], and a capacity of 5l., the Plastic-solid test piece with a size of 100x100x40mm (a volume of 0.4l.) was sunk, the capacity V (liter) which the water surface at this time shows was measured, and it asked for voidage by the formula (1).

[0051]

$$\{1 - (V-3)/0.4\} \times 100\% \dots \text{Formula (1)}$$

[0052] The Plastic-solid weight A was measured immediately after <water-content> fabrication, the Plastic-solid weight B after leaving this Plastic solid within 80-degree C oven for 12 hours and leaving it in the room of the room temperature of 23 degrees C and 55% of humidity for 12 hours was measured, and it asked for the water content by the formula (2).

[0053]

$$\{(A-B)/B\} \times 100\% \dots \text{Formula (2)}$$

[0054] The foaming object taken out from the inside of a <contraction deformation at time of fabrication> type was left in temperature of 20 degrees C, and the appearance of 30 minutes after was judged visually.

Nothing: Hold the formal configuration.

\*\*: There is contraction deformation of a camber, a crater, etc. and it is not a formal configuration.

[0055] The test piece with a <weld examination> length of 200mm, a width [ of 30mm ], and a thickness of 12.5mm was produced, the test piece was bent to 90 degrees in accordance with the periphery of a cylinder with a diameter of 50mm, and it judged on the following criteria.

O : 80% or more of a test piece total cannot be broken.

x: The thing exceeding 20% of a test piece total breaks.

The above result was shown in Table 1.

[0056]

[Table 1]  
(表1)

	実施例1	実施例2	実施例3	比較例1	比較例2	比較例3	比較例4
芯層の樹脂 融点(℃)	ET-PR 153	ET-PR 153	ET-PR 153	ET-PR 153	ET-PR 153	ET-PR 153	ET-PR 153
被覆層の樹脂 融点(℃)	M-LLDPE 91	M-LLDPE 91	LLDPE 123	M-LLDPE 91	ET(3.5)-PR 142	—	M-LLDPE 91
平均嵩密度(kg/m <sup>3</sup> )	17	17	17	17	17	17	17
L/D比	0.9	1.9	1.2	0.4	1.3	1.1	0.9
芯層の状態	発泡	発泡	発泡	発泡	発泡	発泡	発泡
被覆層の状態	実質非発泡	実質非発泡	実質非発泡	実質非発泡	発泡	—	実質非発泡
加熱媒体	空気	空気	空気	空気	空気	空気	水蒸気
加熱成形温度(℃)	120	110	125	120	125	125	120
圧縮率(%)	40	10	30	40	30	30	40
成形体密度(kg/m <sup>3</sup> )	28	18	24	28	融着せず	融着せず	30
空隙率(%)	1<	35	10	1<	測定不可	測定不可	1<
含水率(重量%)	無	無	無	無	測定不可	測定不可	8
成形時の収縮変形	無	無	無	無	測定不可	測定不可	有
融着試験	○	○	○	×	測定不可	測定不可	○

ET-PR: エチレン1.5重量%—プロピレンランダム共重合体

M-LLDPE: メタロセン触媒で重合された直鎖状低密度ポリエチレン

LLDPE: 直鎖状低密度ポリエチレン

ET(3.5)-PR: エチレン3.5重量%—プロピレンランダム共重合体

[0057] About the examples 1-3 of this invention, there was no water, and there was also no contraction deformation at the time of fabrication into the opening of a foaming resin particle, or a particle, and weld intensity was also higher than this \*\*.

[0058]

[Effect of the Invention] According to this invention, it excels in configuration stability and the manufacture method of a thermoplastics foaming object that the weld intensity in a foaming resin particle is high can be offered.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

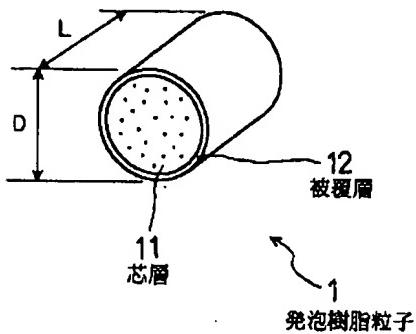
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

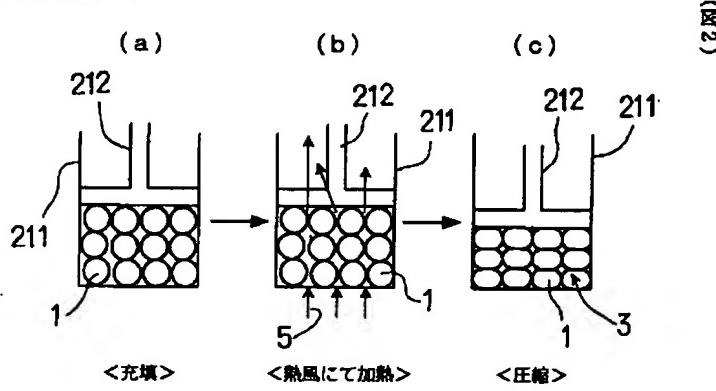
DRAWINGS

---

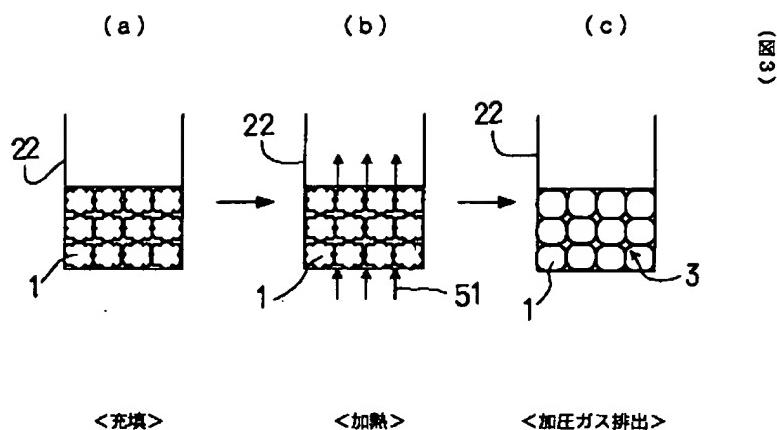
[Drawing 1]  
(図1)



[Drawing 2]



[Drawing 3]



[Translation done.]

(19)日本国特許庁 (JP)

(12)公開特許公報 (A)

(11)特許出願公開番号

特開2000-894

(P 2000-894 A)

(43)公開日 平成12年1月7日(2000.1.7)

(51) Int.Cl.  
B29C 67/20  
C08J 3/12  
// B29K101:12  
105:04

識別記号  
CES

F I  
B29C 67/20  
C08J 3/12

E 4F070  
Z 4F212

マーク(参考)

審査請求 未請求 請求項の数 3 ○ L (全7頁)

(21)出願番号

特願平10-168327

(22)出願日

平成10年6月16日(1998.6.16)

(71)出願人 599050893

三菱化学フォームプラスティック株式会社  
東京都千代田区有楽町一丁目10番1号

(72)発明者 横山 正明

三重県四日市市川尻町1000番地 三菱化学  
ピーエーエスエフ株式会社内

(72)発明者 大桑 輝也

三重県四日市市川尻町1000番地 三菱化学  
ピーエーエスエフ株式会社内

(74)代理人 100079142

弁理士 高橋 祥泰

最終頁に続く

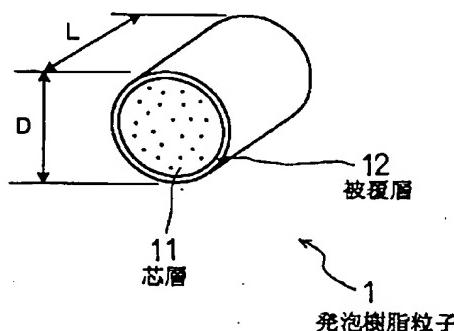
(54)【発明の名称】熱可塑性樹脂発泡成形体の製造方法

(57)【要約】

【課題】 形状安定性に優れ、且つ発泡樹脂粒子内の融着強度が高い、熱可塑性樹脂発泡成形体の製造方法を提供する。

【解決手段】 結晶性の熱可塑性樹脂からなる発泡状態の芯層11と、芯層11を被覆する実質的に非発泡状態の被覆層12とからなるとともに、被覆層は、熱可塑性樹脂より融点が低いかまたは実質的に融点を示さないエチレン系重合体を含有し、粒子の長径Lと短径DとのL/D比が0.5~3である発泡樹脂粒子1を準備する工程と、発泡樹脂粒子を成形型211内に入れて、熱風5により加熱成形することにより発泡樹脂粒子を互いに融着させた熱可塑性樹脂からなる発泡成形体3を得る工程とからなる。熱風5は水蒸気圧が5kPa以下の乾燥ガスを用いる。

(図1)



## 【特許請求の範囲】

【請求項1】 結晶性の熱可塑性樹脂からなる発泡状態の芯層と、該芯層を被覆する実質的に非発泡状態の被覆層とからなるとともに、該被覆層は、上記熱可塑性樹脂より融点が低いかまたは実質的に融点を示さないエチレン系重合体を含有し、且つ粒子の長径Lと短径DとのL/D比が0.5～3である発泡樹脂粒子を準備する工程と、該発泡樹脂粒子を成形型内に入れて、熱風により加熱成形することにより上記発泡樹脂粒子を互いに融着させた熱可塑性樹脂発泡成形体を得る工程とからなり、且つ上記熱風は水蒸気圧が5kPa以下の乾燥ガスを用いることを特徴とする熱可塑性樹脂発泡成形体の製造方法。

【請求項2】 請求項1において、上記発泡樹脂粒子の加熱成形は、該発泡樹脂粒子の嵩容積を50～95%に圧縮して、見かけ密度を高くした状態で行うことを特徴とする熱可塑性樹脂発泡成形体の製造方法。

【請求項3】 請求項1又は2において、上記発泡樹脂粒子の加熱成形は、125℃以下の温度で行うことを特徴とする熱可塑性樹脂発泡成形体の製造方法。

## 【発明の詳細な説明】

## 【0001】

【技術分野】 本発明は、断熱材、緩衝材、包装容器、吸音材、浮揚材等に用いられる熱可塑性樹脂発泡成形体の製造方法に関する。

## 【0002】

【従来技術】 断熱材、緩衝材、包装容器、吸音材、浮揚材には、ポリスチレン、ポリエチレン、ポリプロピレン等の熱可塑性樹脂からなる発泡成形体が用いられている。かかる発泡成形体は、独立気泡構造を有し、軽量で断熱性や緩衝性が良好である。これらの発泡樹脂粒子はこの断熱性ゆえに、加熱成形時に均一に加熱されにくく、加熱媒体として熱容量の大きい水蒸気を用いて発泡成形体を製造している点が共通している。発泡成形体は、発泡樹脂粒子を金型に入れ加熱し、粒子表面を融着させることにより成形されたものである。樹脂粒子同志を融着させるためには、従来、蒸気圧としてポリスチレンでは0.1MPa以下、ポリエチレンでは0.2MPa以下、ポリプロピレンで0.5MPa以下の水蒸気が用いられていた。

## 【0003】

【解決しようとする課題】 しかしながら、上記従来のシステム加熱による融着法では、加熱融着時に、発泡樹脂粒子の空隙又は粒子の中に水分が気体状態で浸入し、この状態で冷却すると水分が気体から液体の状態に凝縮し、体積収縮を起こす。このため、発泡樹脂粒子の空隙又は粒子の中が減圧状態になり、かかる粒子からなる発泡成形体が収縮、変形することになり、形状安定性が悪く、型通りの成形体が得られにくいという問題がある。また、発泡成形体においては、発泡樹脂粒子が充分に融

着して、機械的強度が高いことも要求される。

【0004】 本発明はかかる従来の問題点に鑑み、形状安定性に優れ、且つ発泡樹脂粒子内の融着強度が高い、熱可塑性樹脂発泡成形体の製造方法を提供しようとするものである。

## 【0005】

【課題の解決手段】 本発明は、結晶性の熱可塑性樹脂からなる発泡状態の芯層と、該芯層を被覆する実質的に非発泡状態の被覆層とからなるとともに、該被覆層は、上記熱可塑性樹脂より融点が低いかまたは実質的に融点を示さないエチレン系重合体を含有し、且つ粒子の長径Lと短径DとのL/D比が0.5～3である発泡樹脂粒子を準備する工程と、該発泡樹脂粒子を成形型内に入れて、熱風により加熱成形することにより上記発泡樹脂粒子を互いに融着させた熱可塑性樹脂発泡成形体を得る工程とからなり、且つ上記熱風は水蒸気圧が5kPa以下の乾燥ガスを用いることを特徴とする熱可塑性樹脂発泡成形体の製造方法である。

【0006】 本発明における熱可塑性樹脂発泡成形体の製造方法は、上記のごとく特定の芯層とこれを被覆する被覆層とからなる発泡樹脂粒子を用いている。そのため、従来加熱媒体として用いられてきたシステム（水蒸気）を全く使用せず、上記の乾燥ガスからなる熱風にて加熱することで発泡成形体を得ることができる画期的方法である。

【0007】 本発明の作用及び効果を説明する。発泡樹脂粒子は、成形型内に入れ、上記の乾燥ガスからなる熱風を用いて所望形状に加熱成形している。そのため、加熱成形時に、発泡樹脂粒子の空隙又は粒子の中には、殆ど水蒸気が浸入しない。それゆえ、従来の欠点であった水蒸気の凝縮による成形体の含水もなくなり、それに伴う成形体の体積収縮も起こらない。よって、本発明の発泡樹脂成形体は形状安定性に優れている。また、寸法及び収縮変形を矯正するための高温養生処理も不要である。しかも、含水もないため、成形後の乾燥処理をしなくてもよく、得られた発泡成形体は断熱性に優れ、サビ発生のおそれもない。また、乾燥ガスによる加熱成形では、従来の発泡樹脂粒子の加熱成形時に用いられていた高圧蒸気圧に耐える従来構造の重量のある金型が不要であり、熱エネルギーの消費量も少ない。

【0008】 また、熱可塑性樹脂からなる表皮と発泡樹脂粒子とを型内で一体成形を行う場合には、水蒸気の水分による影響が無くなるため、熱可塑性樹脂からなる表皮と発泡樹脂粒子とが強固に融着する。従って、本発明により得られた発泡成形体は融着強度が高く、機械的強度に優れている。また、表皮として熱可塑性樹脂からなる織布又は不織布状を使用した場合には、蒸気アイロン掛け時に発生する表皮表面の毛倒れが無くなり、色合い、手触り等の外観も良好で、乾燥の後工程も不要となり、工業的に有利である。

【0009】その他、表皮としては、フィルム状、シート状、真空成形品、インジェクション成形品などを発泡樹脂粒子と一体成形することもできる。

【0010】また、発泡樹脂粒子は、結晶性の熱可塑性樹脂からなる独立気泡体である芯層と、エチレン重合体を含有する実質的にフィルム状の被覆層とから構成されている。そのため、型内に充填された発泡樹脂粒子間の空隙に、熱容量の小さい熱風を通過させることにより、被覆層よりも融点が高い芯層の発泡力を抑えながら、被覆層が融着するのに必要な温度まで発泡樹脂粒子を加熱でき、その後、芯層が保有する圧縮反力を有効に活用して発泡樹脂粒子を融着させて発泡成形体を製造することができる。

【0011】次に、本発明の詳細について説明する。

(発泡樹脂粒子の準備) 本発明における発泡樹脂粒子は、発泡状態の芯層と実質的に非発泡状態の被覆層とから構成される複合構造を有する。発泡状態の芯層は、例えば、独立気泡構造又は連続気泡構造を有する。この内、独立気泡構造を有することが好ましい。その理由は、独立気泡構造は、加熱成形時の芯層の圧縮反力が高く、低密度でも圧縮強度が高いからである。芯層の独立気泡率は50%以上が好ましく、更には70%以上であることが好ましい。これにより、加熱成形時の芯層の圧縮反力が更に高くなり、また低密度でも圧縮強度が高い発泡成形体を得ることができる。被覆層は、非発泡状態である。被覆層は、厚さ1~150μmのフィルム状の熱可塑性樹脂層であることが好ましい。

【0012】芯層は、結晶性の熱可塑性樹脂にて構成される。かかる結晶性の熱可塑性樹脂としては、例えば、ポリプロピレン系樹脂、ポリブテン系樹脂、ポリメチルペンテン系樹脂、ポリエステル系樹脂、ポリアミド系樹脂、フッ素系樹脂、結晶性のスチレン系樹脂などが挙げられる。この中でも、プロピレン単独重合体、プロピレンとプロピレン以外のα-オレフィンとのランダム共重合体やブロック共重合体が好ましい。これにより、安価でリサイクル性に優れ、軽量で断熱性及び緩衝性に優れた発泡成形体を得ることができる。

【0013】被覆層は、実質的に非発泡状態である。

「実質的に非発泡状態」とは、厚さ1~150μmと薄く、気泡構造のないフィルム状態を意味する。また、被覆層は、上記熱可塑性樹脂より融点が低いか、または、実質的に融点を示さないエチレン系重合体を含有する。かかる低融点のエチレン系重合体としては、高压法低密度ポリエチレン、直鎖状低密度ポリエチレン、直鎖状超低密度ポリエチレンの他、酢酸ビニル、不飽和カルボン酸エステル、不飽和カルボン酸、ビニルアルコール等とエチレンの共重合体が挙げられる。

【0014】「実質的に融点がない」とは、示差走査熱量計にて昇温した際に融解ピークが現れない結晶性のない樹脂を意味する。かかる実質的に融点がないエチレン

系重合体としては、例えば、エチレン・プロピレンゴム、エチレン・プロピレン・ジエンゴム、エチレン・アクリルゴム、塩素化ポリエチレンゴム、クロロスルホン化ポリエチレンゴム等のゴム・エラストマーが挙げられる。これらのエチレン系重合体は、単独使用の他、2種以上の組成物として使用することができる。

【0015】上記のエチレン系重合体の中では、高压法低密度ポリエチレン、直鎖状低密度ポリエチレン、直鎖状超低密度ポリエチレンが好ましい。中でもメタロセン触媒を使用して重合された直鎖状低密度ポリエチレン、直鎖状超低密度ポリエチレンが最も好ましい。

【0016】被覆層を構成する上記のエチレン系重合体の融点は実質的ないか、又は融点があったとしても125℃以下であることが好ましい。その理由は、発泡樹脂粒子を成形する際の加熱温度をより低温に設定することができるからである。

【0017】更に、被覆層としては、芯層を構成する熱可塑性樹脂に対し、15℃以上低い融点のエチレン系重合体を選択して使用するのが好ましい。エチレン系重合体と熱可塑性樹脂の上記の融点差は、好ましくは20℃~100℃の範囲である。上記の融点差が15℃未満の場合、芯層の熱可塑性樹脂を発泡させる条件下においては、エチレン系重合体から成る被覆層が発泡する虞がある。

【0018】また、上記の被覆層は、上記エチレン系重合体と、芯層と同種の結晶性熱可塑性樹脂との混合物であることが好ましい。これにより、被覆層と芯層との接着性が向上する。被覆層における熱可塑性樹脂の配合割合は、エチレン系重合体100重量部に対し、1~100重量部の範囲から選択されることが好ましい。熱可塑性樹脂の配合割合が1重量部未満の場合には、芯層と被覆層との接着性向上の効果が低くなるおそれがある。また、100重量部を超える場合には、被覆層の海島形態が変化し、熱可塑性樹脂が連続した海の相を構成することとなり、成形時の加熱温度があまり低くならない。更に、熱可塑性樹脂の混合割合は、エチレン系重合体100重量部に対し、1~50重量部の範囲であることが望ましい。これにより、芯層と被覆層との接着性が向上し、また成形時の加熱温度を低くすることができる。

【0019】発泡樹脂粒子において、被覆層の厚さは1~150μmであることが好ましい。被覆層の厚さが1μm未満の場合には、成形の際、加熱温度を十分に低下させる効果が少ない。一方、被覆層の厚さが150μmを超える場合には、成形の際、加熱温度は下げる事が出来るものの、被覆層における実質的に非発泡性部分の割合が大きく、成形体の機械的強度が発泡倍率の割には低くなる傾向にある。更には被覆層の厚みは10~100μmであることが好ましい。これにより、成形の際に加熱温度を下げることができ、かつ発泡成形体の機械的強度を高めることができる。

【0020】図1に示すごとく、本発明の発泡樹脂粒子1の長径Lと短径DとのL/D比は0.5~3である。0.5未満の場合には、被覆層12の表面積が少なくなり、融着不良をもたらす。また、3を超える場合には、粒子形状が細長となり、充填効率が悪化し、成形不良や形状安定性の低下をもたらす。L/D比は、1.5~3と比較的大きい場合には空隙の多い成形体を得やすくなるが、成形性の点から、0.8~2であることが好ましい。

【0021】上記発泡樹脂粒子1は、例えば、図1に示すごとく、結晶性の熱可塑性樹脂から成る芯層11と、熱可塑性樹脂より融点が低いか、または、実質的に融点を示さないエチレン系重合体を含有する被覆層12にて構成される複合体粒子に揮発性発泡剤を含浸させた後、加熱発泡して得られる。

【0022】上記の揮発性発泡剤としては、プロパン、ブタン、ペンタン、ヘプタン、シクロヘキサン、シクロヘキサン等の低級脂肪族炭化水素類、ジクロロジフロロメタン、トリクロロモノフロロメタン等のハロゲン化炭化水素、窒素、空気、炭酸ガス等の無機ガス等が挙げられ、これらは、単独または2種類以上組合せて使用される。

【0023】発泡樹脂粒子の原料となる複合体粒子の具体的な製造方法としては、次の各方法が使用される。例えば、特公昭41-16125号公報、同43-23858号公報、同44-29522号公報、特開昭60-185816号公報などに記載の鞘芯型の複合ダイが使用される。この場合、2基の押出し機が使用され、一方の押出し機で芯層を構成する熱可塑性樹脂を溶融混練し、他方の押出し機で被覆層を構成するエチレン系重合体組成物を溶融混練した後、ダイで熱可塑性樹脂を芯層とし、エチレン系重合体組成物を被覆層として鞘芯型の複合体を吐出させる。

【0024】次いで、この様にして得られた複合体をカットして0.1~10mgの複合体粒子とする。複合体粒子の重量が0.1mg未満の場合は、成形加工の加熱温度を効果的に低下させる被覆層比率が高くなるため、得られる発泡成形体の機械的強度が低下する。一方、複合体粒子の重量が10mgを超える場合は、成形時の金型への充填性が悪化しやすい。

【0025】上記の鞘芯型の複合体粒子に揮発性発泡剤を含浸した後、加熱により発泡させる。かかる加熱発泡方法としては、具体的には、例えば、特公昭49-2183号公報、同56-1344号公報、西ドイツ特開第1285722号公報、同第2107683号公報などに記載の方法を使用し得る。

【0026】この場合、密閉容器内に揮発性発泡剤と共に鞘芯型の複合体粒子を入れ、芯層の結晶性樹脂の軟化温度以上に加熱する共に、複合体粒子に揮発性発泡剤を含浸させる。その後、密閉容器内の内容物を密閉容器よ

り低圧の雰囲気に放出した後、乾燥処理することにより、発泡樹脂粒子が得られる。

【0027】複合体粒子の発泡時の加熱温度は、通常、芯層の熱可塑性樹脂の軟化温度以上とされるが、被覆層のエチレン系重合体の融点（組成物の場合は主成分の融点）より高い温度にするのが好ましい。また、本発明では、密閉容器内で複合体粒子同士が相互に融着しない様にするため、攪拌装置を付備することが好ましい。

【0028】複合体粒子の加熱発泡時には、複合体粒子の分散媒として、水、アルコール類などを使用することが好ましい。さらに、複合体粒子が分散媒に均一に分散する様に、酸化アルミニウム、第三リン酸カルシウム、ピロリン酸マグネシウム、酸化亜鉛などの難水溶性の無機物質、ポリビニルピロリドン、ポリビニルアルコール、メチルセルロース等の水溶性保護コロイド、ドデシルベンゼンスルホン酸ナトリウム、 $\alpha$ -オレフィンスルホン酸ナトリウム等の陰イオン性界面活性剤を単独または2種類以上混合して使用するのが好ましい。

【0029】複合体粒子は、低圧雰囲気に放出することが好ましい。これにより、複合体粒子の熱可塑性樹脂が発泡して、発泡状態の芯層とこれを被覆する被覆層とからなる発泡樹脂粒子を得ることができる。低圧の雰囲気に複合体粒子を放出する際、当該放出を容易にするため、上記と同様な無機ガス又は揮発性発泡剤を外部より密閉容器に導入して密閉容器内の圧力を一定に保持することが好ましい。

【0030】発泡樹脂粒子は、その粒子のカット断面の状態から、芯層の熱可塑性樹脂が独立気泡構造の発泡状態を呈し、一方、被覆層のエチレン系重合体が実質的に非発泡のフィルム状態となっている。

【0031】（発泡樹脂粒子の加熱成形）発泡樹脂粒子は、熱風にて加熱成形する。ここで、熱風は、電熱ヒーター、蒸気ヒーターなどの加熱手段により空気を加熱して得られる。また、プロアー、圧縮空気を利用して供給すると、発泡樹脂粒子を効率よく加熱することができる。また、熱風を回収、循環する方式を利用することにより熱エネルギーのロスを少なくすることができます。

【0032】熱風は水蒸気圧が5kPa以下の乾燥ガスを用いる。これにより、加熱成形時に発泡樹脂粒子の空隙又は粒子の中に水蒸気が侵入することを防止でき、発泡成形体の形状安定性を確保できる。

【0033】また、加熱成形時における、発泡樹脂粒子の温度は125°C以下であることが好ましい。125°Cを超える場合には、熱風の発生装置が大きく、高価なものになり、工業的なメリットがなくなり、また型内の発泡樹脂粒子を均一に加熱コントロールすることも、より難しいものになるおそれがあるからである。

【0034】発泡樹脂粒子を加熱成形する際には、発泡樹脂粒子の圧縮状態は、成形体に要求される物性により適宜設定するが、圧縮を小さくすれば、発泡樹脂粒子同

土の接触面積が少ない空隙のある成形体が得られる。また、加熱と圧縮とは、いずれを先に行っても良い。

【0035】発泡樹脂粒子の加熱成形は、該発泡樹脂粒子の嵩容積を50～95%に圧縮して、見かけ密度を高くした状態で行なうことが好ましい。50%以上に圧縮する場合には、殆ど空隙のない状態の発泡成形体が得られることになり、発泡成形体の密度をただ単に大きくするだけで意味がない。95%未満に圧縮する場合には、発泡樹脂粒子同士の接触面積がより小さくなり融着強度の弱い発泡成形体になる。

【0036】発泡樹脂粒子の加熱成形の具体的方法としては、例えば、図2に示すごとく、通気性の下型211内に発泡樹脂粒子1を充填した後(a)、下型211内に充填された発泡樹脂粒子1間の間隙に熱風5を通過させながら、発泡樹脂粒子1の表面温度を、発泡樹脂粒子を構成する被覆層が融着するに必要な温度まで加熱し(b)、その後上型212により発泡樹脂粒子1の嵩容積を50～95%に圧縮して(c)発泡成形体3を得る方法がある。

【0037】また、図3に示すごとく、密閉性の金型22の中に発泡樹脂粒子1の嵩容積を50～95%に圧縮し保持した状態で発泡樹脂粒子を入れて(a)、その中に熱風加圧ガス51を圧入して、発泡樹脂粒子1間の間隙に熱風加圧ガス51を通過させて、発泡樹脂粒子1の表面温度を、発泡樹脂粒子を構成する被覆層が融着するに必要な温度まで加熱して(b)、次いで、熱風加圧ガス51を排出して発泡樹脂粒子1の圧縮状態を回復することにより発泡成形体3(c)を得る方法がある。

【0038】本発明においては、発泡樹脂粒子の性状や発泡成形体の形状、密度等を考慮して成形条件を選択するが、揮発性発泡剤または無機ガスで予め処理して、2次発泡力を高めた発泡樹脂粒子を使用すれば、より密度の小さい発泡成形体が得られ易くなる。また、通気性のある凸凹一対の型に代えて、通気性のあるベルトを用いることで板状発泡成形体の製造も可能である。

【0039】上記製造方法により得られる熱可塑性樹脂発泡成形体としては、結晶性の熱可塑性樹脂からなる発泡状態の芯層と、該芯層を被覆する被覆層とから構成されている発泡樹脂粒子を加熱成形してなる熱可塑性樹脂発泡成形体であって、上記被覆層は、上記熱可塑性樹脂より融点が低いか、または、実質的に融点を示さないエチレン系重合体を含有し、且つ、非発泡状態であることを特徴とする熱可塑性樹脂発泡成形体である。

【0040】本発明により得られた熱可塑性樹脂発泡成形体は、例えば、断熱材、緩衝材、包装容器、吸音材、浮揚材、工業部材等に用いられる。また、熱可塑性樹脂発泡成形体は、熱可塑性樹脂からなる、織布、不織布、フィルム、シート、真空成形品、インジェクション成形品との一体成形品等にも用いられる。

【0041】

【発明の実施の形態】本発明の実施形態例について、実施例1～3を、比較例1～4と比較しつつ説明する。

#### 実施例1

内径40mmの単軸押出し機を使用してエチレン含量

1.5重量%のエチレン・プロピレンランダム共重合体(融点153℃)を混練し、内径25mmの単軸押出し機を使用して密度0.895のメタロセン触媒で重合された直鎖状低密度ポリエチレン(融点91℃)を混練した。次いで、直径1.5mmのダイオリフィースを有するダイから、エチレン・プロピレンランダム共重合体を芯層とし、直鎖状低密度ポリエチレンを被覆層としてストランドを押し出した。

【0042】さらに、このストランドを、水槽を通して冷却した後、1.2mgに切断した。この複合体粒子の断面を位相差顕微鏡により観察したところ、厚さ30μmの直鎖状低密度ポリエチレンがエチレン・プロピレンランダム共重合体を被覆していた。

【0043】次に、密閉容器内に上記の複合体粒子100重量部、水250重量部、粒径0.3～0.5μmの第三リン酸カルシウム1.0重量部およびドデシルベンゼンスルホン酸ナトリウム0.007重量部を仕込み、次いで、攪拌下にてブタン20重量部を密閉容器内へ供給した。内容物を充填率62%で充填した後、一時間かけて145℃まで昇温して同温度で30分間保持した。

【0044】その後、密閉容器の底部にある放出孔の弁を開くと共に外部より密閉容器内の気相部へ窒素ガスを導入し、容器内の圧力を保持しつつ内容物を大気圧下へ放出して発泡樹脂粒子を得た。こうして得られた発泡樹脂粒子は、平均嵩密度17kg/m<sup>3</sup>、平均気泡径120μmであり、発泡樹脂粒子同士のブロッキングもなかった。

【0045】この発泡樹脂粒子の断面を位相差顕微鏡にて観察したところ、芯層のエチレン・プロピレンランダム共重合体は、独立気泡の発泡状態にあり、一方、直鎖状低密度ポリエチレンは、実質的に非発泡のフィルム状態で、エチレン・プロピレンランダム共重合体の発泡状態の芯層を被覆していた。発泡樹脂粒子の長径Lと短径DとのL/Dは、0.9である。

【0046】この発泡樹脂粒子を40℃の乾燥室にて完全に乾燥し、通気性のある凸凹一対の型内に、この発泡樹脂粒子を充填した後、型内に充填された発泡樹脂粒子間の間隙に熱風を通過させて、発泡樹脂粒子の表面温度を120℃に加熱し、次いで、型内容積を60%に減容した状態で、発泡樹脂粒子を融着させた。その後、空気にて冷却し、型内より発泡成形体を取出した。発泡成形体は、密度が28kg/m<sup>3</sup>であり、大きさは縦200mm、幅300mm、厚み40mmであり、含水もなく、収縮変形のない型通りの形状であった。

【0047】上記の発泡成形体から、長さ200mm、巾30mm、厚さ12.5mmの試験片20片を作製

し、直径50mmの円筒の円周に巻き、90°の角度まで曲げたところ、試験片の80%以上が割れなかった。

【0048】実施例2、3、比較例1~4

実施例2、3、比較例1~4においては、表1に示すごとく、芯層の樹脂及び状態、被覆層の樹脂及び状態、平均嵩密度、L/D比、加熱媒体、加熱成形温度、圧縮率を変えて、発泡成形体を製造した。その他は、実施例1と同様に製造した。

【0049】上記実施例1~3及び比較例1~4の物性について、以下の方法により測定した。

<融点>示差走査熱量計(DSC)により測定した。先ず、3~5mgの樹脂をその結晶が融解する温度まで昇

$$\{1 - (V-3) / 0.4\} \times 100\% \dots \text{式(1)}$$

【0052】<含水率>成形直後に成形体重量Aを測定し、同成形体を80℃のオーブン内で12時間放置し、室温23℃、湿度55%の部屋で12時間放置した後の成形体重量Bを測定し、式(2)により含水率をもとめた。

【0053】

$$\{(A-B) / B\} \times 100\% \dots \text{式(2)}$$

【0054】<成形時の収縮変形>型内より取出した発泡成形体を温度20℃に放置し、30分後の外観を目視にて判定した。

無：型通りの形状を保持している。

(表1)

	実施例1	実施例2	実施例3	比較例1	比較例2	比較例3	比較例4
芯層の樹脂 融点(℃)	ET-PR 153	ET-PR 153	ET-PR 153	ET-PR 153	ET-PR 153	ET-PR 153	ET-PR 153
被覆層の樹脂 融点(℃)	M-LLDPE 91	M-LLDPE 91	LLDPE 123	M-LLDPE 91	ET(3.5)-PR 142	—	M-LLDPE 91
平均嵩密度(kg/m³)	17	17	17	17	17	17	17
L/D比	0.9	1.9	1.2	0.4	1.3	1.1	0.9
芯層の状態	発泡	発泡	発泡	発泡	発泡	発泡	発泡
被覆層の状態	実質非発泡	実質非発泡	実質非発泡	実質非発泡	発泡	—	実質非発泡
加熱媒体	空気	空気	空気	空気	空気	空気	水蒸気
加熱成形温度(℃)	120	110	125	120	125	125	120
圧縮率(%)	40	10	30	40	30	30	40
成形体密度(kg/m³)	28	19	24	28	融着せず	融着せず	30
空隙率(%)	1<	35	10	1<	測定不可	測定不可	1<
含水率(重量%)	無	無	無	無	測定不可	測定不可	8
成形時の収縮変形	無	無	無	無	測定不可	測定不可	有
融着試験	○	○	○	×	測定不可	測定不可	○

ET-PR:エチレン1.5重量%一プロピレンランダム共重合体

M-LLDPE:メタロセン触媒で重合された直鎖状低密度ポリエチレン

LLDPE:直鎖状低密度ポリエチレン

ET(3.5)-PR:エチレン3.5重量%一プロピレンランダム共重合体

【0057】同表より、本発明の実施例1~3については、発泡樹脂粒子の空隙又は粒子の中に含水はなく、成形時の収縮変形もなく、かつ融着強度も高かった。

【0058】

【発明の効果】本発明によれば、形状安定性に優れ、且つ発泡樹脂粒子内の融着強度が高い、熱可塑性樹脂発泡成形体の製造方法を提供することができる。

【図面の簡単な説明】

【図1】本発明における、発泡樹脂粒子の斜視図。

【図2】本発明における、上型及び下型を用いる加熱成形方法を示す説明図。

【図3】本発明における、熱風加圧ガスを用いる加熱成形方法を示す説明図。

【符号の説明】

1...発泡樹脂粒子、

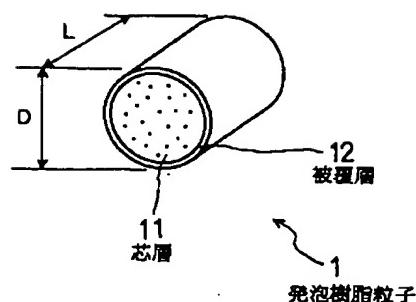
50 11...芯層、

12. . . 被覆層.

3. . . 発泡成形体.

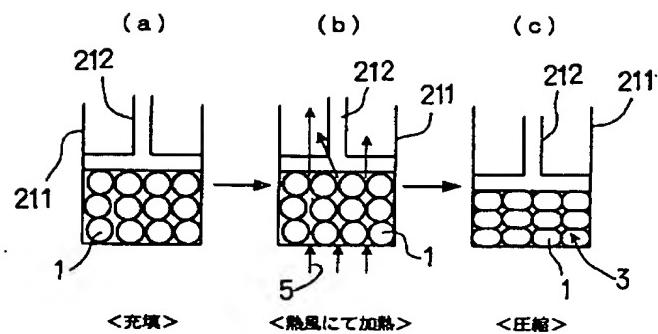
【図1】

(図1)



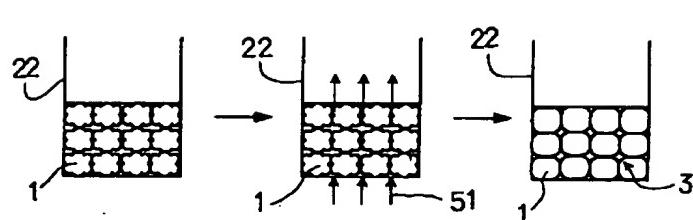
【図2】

(図2)



【図3】

(図3)



フロントページの続き

Fターム(参考) 4F070 AA16 AE12 DA11 DC02 DC05  
 4F212 AA09 AB02 AD05 AE06 AG03  
 AG20 AK01 UA02 UB01 UC02  
 UF01 UF21 UC05 UN21